

Partial Translation of JP 2001-185145

"METHOD OF MANUFACTURING POSITIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY"

[CLAIMS]

[Claim 1] A method of manufacturing a positive electrode material for a lithium secondary battery comprising a lithium insertion compound having a spinel structure and being represented by the general formula $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ (where $0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$; M is nickel or mainly composed of nickel and added with aluminum or one or two or more metal elements selected from transition metal elements), the method comprising:

producing a mixed hydroxide with a coprecipitation method, wherein the mixed hydroxide includes manganese and the metal M at a predetermined ratio; and

mixing the mixed hydroxide with a lithium compound and heat-treating the obtained mixture at a temperature from 700°C to 900°C.

[Claim 2] The method of manufacturing a positive electrode material for a lithium secondary battery according to claim 1, wherein the transition metal elements are copper, cobalt, chromium or iron.

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-185145

(43)Date of publication of application : 06.07.2001

(51)Int.Cl.

H01M 4/58
C01G 45/00

(21)Application number : 11-368613

(71)Applicant : NIKKO MATERIALS CO LTD

(22)Date of filing : 27.12.1999

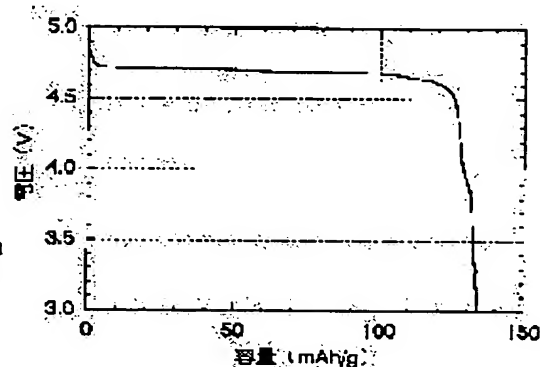
(72)Inventor : KOHIRO KENJI
FUJIHIRA YOSHIHISA

(54) METHOD OF MANUFACTURING POSITIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To establish a method of manufacturing for an NiO-free $\text{Li}(1+x)\text{Mn}(2-x-y)\text{MyO}_4$ -based spinel compound.

SOLUTION: A method of manufacturing a positive electrode material for a lithium secondary battery consists of a lithium-inserted compound having a spinel structure of a general formula $\text{Li}(1+x)\text{Mn}(2-x-y)\text{MyO}_z$ (wherein, $0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.96 \leq z \leq 4.06$); M is nickel, or uses the nickel as its essential constituent and one or two or more metals selected from aluminum or a transition metal element is added to the nickel). Where, a mixed hydroxide of manganese and the metal M with the given ratio is manufactured by the coprecipitation method. The mixed hydroxide is mixed with a lithium compound. A heat treatment is then applied to the resulting mixture at 700 to 900° C.



* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]General formula $\text{Li}_{(1+x)} \text{Mn}_{(2-x-y)} \text{M}_y \text{O}_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$, and M)

what added one sort or two sorts or more of metal which uses nickel or nickel as an essential ingredient, and is chosen as this from aluminum or a transition metal element -- expressing -- in a manufacturing method of a positive electrode material for lithium secondary batteries which comprises a lithium inserted compound of Spinel structure expressed, A manufacturing method of a positive electrode material for lithium secondary batteries producing manganese of a predetermined ratio, and mixed hydroxide of the metal M with a coprecipitation method, mixing this with a lithium compound, and heat-treating at 700 ** - 900 **.

[Claim 2]A manufacturing method of the positive electrode material for lithium secondary batteries according to claim 1, wherein the above-mentioned transition metal elements are copper, cobalt, chromium, and iron.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the LiMn_2O_4 system spinel compound which are a positive electrode material for lithium secondary batteries, especially a high-tension positive electrode material.

[0002]Since a lithium secondary battery has a high energy density as compared with the conventional rechargeable battery, have spread as cells for electronic equipment, such as a cellular phone, a portable video camera, and a notebook sized personal computer, but. The use as a distributed type power supply of an electromobile or an ordinary home is expected in the future, and the research and development for obtaining high capacity and an efficient cell further are done briskly.

[0003]Although LiCoO_2 is mainly used for the positive active material for lithium secondary batteries marketed now, since there are few deposits of cobalt itself, it has a fault in respect of adequate supply and cost bad [thermal stability].

[0004]Research of the nickel cobalt multiple oxide which is excellent in the economic target with abundant resources as what changes to this is done briskly. However, composition in the atmosphere is difficult for this compound, and oxygen environment is needed, and also. In order that nickel may tend to occupy Li site, there are be [many technical technical problems / and] problems that thermal stability is still worse than LiCoO_2 in manufacturing this material with sufficient characteristic by a practical method.

[0005]Since it is such, even if it compares with nickel, the LiMn_2O_4 system spinel compound also in cost whose resource quantity is abundant and advantageous attracts attention. Although this spinel compound is excellent in thermal stability and it is extremely stable, the cycle characteristic of the rechargeable battery using this is bad, and poses a practical big problem.

[0006]The trial which replaces some manganese by other elements in order to improve this fault is performed briskly. If manganese is replaced by other transition metal elements in relation to this trial, it is known that 5V field will appear in addition to 4V field of the conventional LiMn_2O_4 system spinel compound. Especially if cell voltage becomes high, when many cells, such as an object for electromobiles, need to be laminated, there is a big merit.

[0007]That is, when voltage goes up, it is because the number of control circuits will become fewer that much if the number of the cells connected in series becomes fewer, so it becomes advantageous in cost.

[0008]as for the thing whose 5V field the amount of substitution of a transition metal element increases and which is alike, follows, spreads and is replaced with divalent like nickel, 5V field becomes about 150 mAh/g and the maximum by $x = 0.5$ of $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$.

[0009]On the other hand, 5V field is replaced with the maximum by trivalent by $x = 1$ like cobalt, chromium, and iron. If the amounts of substitution, such as a transition metal element, are increased gradually also experimentally, the tendency which 5V field increases gradually will be seen. However, if a constant rate with the amounts of substitution, such as a transition metal

element, is exceeded, the capacity of 5V field will come to decrease [not increasing more than it, and].

[0010] This is because it becomes impossible to maintain Spinel structure and stops dissolving thoroughly from the difference in the ion radius of manganese and other elements, if the amounts of substitution, such as a transition metal element, increase.

[0011] Therefore, the direction which adopted the element in which the 5V field greatest by $x=0.5$ is obtained like nickel is [using chromium etc. rather than] advantageous. Some reports that 5V field of 90 or more mAh/g was obtained by nickel substitution actually exist (for example, J. Power Sources 68 (1997) 604).

[0012] However, if a manganese compound, a nickel compound, and a lithium compound are mixed and heat-treated when it is nickel substitution, it will become $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{Ni}_y\text{O}_4$ of Spinel structure, and a mixture of NiO of rhombohedron structure. In order to keep NiO from remaining only by Spinel structure, it must carry out to less than $x=0.2$, but 5V field sufficient in this is not obtained.

[0013] Then, after carrying out low-temperature composition with wet process, such as a sol gel process, the method of heat-treating at an elevated temperature, etc. are examined (J. Electrochem.Soc., Vol143-1607 (1996)).

[0014] However, generally the spinel compound which carried out wet composition has low tap ** density, and when it is used as a battery material, there is a problem that the volume energy density of a cell becomes low.

[0015]

[Problem(s) to be Solved by the Invention] This invention is what solved the above-mentioned problem, and the purpose of this invention is the metal M (M) so much about Mn. what added one sort or two sorts or more of metal which uses nickel or nickel as an essential ingredient, and is chosen as this from aluminum or a transition metal element -- expressing -- the $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_4$ system (especially) which does not contain replaced NiO It is establishing the method of manufacturing a $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ spinel compound.

[0016]

[Means for Solving the Problem] A result of having examined wholeheartedly a manufacturing method of $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ in order that this invention persons might attain the above-mentioned purpose, It found out that NiO does not remain by producing manganese of a predetermined ratio, and mixed hydroxide of the metal M with a coprecipitation method, and heat-treating this with a lithium compound.

[0017] It is based on this knowledge and this invention is (1) general-formula $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$, and M). what added one sort or two sorts or more of metal which uses nickel or nickel as an essential ingredient, and is chosen as this from aluminum or a transition metal element -- expressing -- in a manufacturing method of a positive electrode material for lithium secondary batteries which comprises a lithium inserted compound of Spinel structure expressed, Manganese of a predetermined ratio and mixed hydroxide of the metal M are produced with a coprecipitation method, A manufacturing method of a positive electrode material for lithium secondary batteries mixing this with a lithium compound and heat-treating at 700 ** - 900 **, (2) The above-mentioned transition metal element provides a manufacturing method of a positive electrode material for lithium secondary batteries of the aforementioned (1) statement being copper, cobalt, chromium, and iron.

[0018]

[Embodiment of the Invention] Hereafter, an embodiment of the invention is described in detail. The greatest feature of this invention is general formula $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$, and M). what added one sort or two sorts or more of metal which uses nickel or nickel as an essential ingredient, and is chosen as this from aluminum or a transition metal element -- expressing -- beforehand in the manufacturing method of the positive electrode material for lithium secondary batteries which comprises the lithium inserted

compound of the Spinel structure expressed, It is in mixing with a lithium compound and heat-treating this, after producing manganese of a predetermined ratio, and mixed hydroxide of the metal M with a coprecipitation method, for example, considering it as compound hydroxide of nickel manganese, compound hydroxide of nickel aluminum manganese, etc.

[0019]Fundamentally, the lithium inserted compound of the Spinel structure expressed with general formula $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ should be able to be manufactured by heat-treating after mixing a manganese compound, the compound of the metal M, and a lithium compound. Therefore, this invention persons tried composition about each of the manganese compound, the compound of the metal M, and the lithium compound using various compounds. For example, as a manganese compound, MnO_2 , Mn_2O_3 , MnCO_3 , $\text{Mn}(\text{NO}_3)_2$, etc. as a compound of the metal M, nickel(OH)₂, NiO, nickel(NO₃)₂, (COO)₂nickel, Co_3O_4 , $\text{Co}(\text{OH})_2$, CoCO_3 , Cr_2O_3 , $\text{Cr}(\text{NO}_3)_3$ and $9\text{H}_2\text{O}$, FeOOH , $\text{Fe}(\text{NO}_3)_3$ and $9\text{H}_2\text{O}$, CuO , $\text{Cu}(\text{OOCCH}_3)_2$ and H_2O , aluminum(OH)₃, etc. were used for Li_2CO_3 , LiOH, etc. as a lithium compound.

[0020]However, when $y = 0.2$ of general formula $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ was exceeded in any case, it turned out that NiO remains. This is in agreement with the contents indicated in literature (J. Electrochem.Soc. and Vol143-1607 (1996)).

[0021]. As one of the reasons NiO remains, $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ and NiO stabilize and exist at 700 ** - 900 ** of the temperature which produces $\text{Li}_{(1+x)}\text{Mn}_2\text{O}_4$. In other words, it may not become $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ single phase thermodynamically. However, although the detailed phase diagram of a Li-Mn-nickel-O system does not exist for example, in the phase diagram of a Mn-nickel-O system, the single phase of nickel_xMn₂O₄ of Spinel structure exists in the quite large field. If it guesses from this, it will be thought also at $\text{Li}_{(1+x)}\text{Mn}_2\text{O}_4$ production temperature that $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ exists in single phase.

[0022]A reactant difference can be considered as another reason nickel-O remains. That is, a lithium compound and a manganese compound react first and a nickel compound reacts after that. If the reactivity of a nickel compound is the worst and $\text{Li}_{(1+x)}\text{Mn}_2\text{O}_4$ is made first, since reaction velocity with a nickel compound is remarkable and slow, NiO will remain. Remains of NiO can be prevented, if this considers it as the right, and a manganese compound and a nickel compound are heat-treated first and it is made to react to a lithium compound after that. If it is made to develop furthermore, a manganese compound and a nickel compound will be mixed very uniformly, and if in contact [good] moreover, the manganese compound and the nickel compound should react before the reaction of a lithium compound and a manganese compound.

[0023]By producing manganese of a predetermined ratio, and mixed hydroxide of the metal M with a coprecipitation method, mixing this with a lithium compound, as a result of inquiring based on such an idea, and heat-treating at 700 ** - 900 **, $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ in which NiO does not remain ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$, and M) what added one sort or two sorts or more of metal which uses nickel or nickel as an essential ingredient, and is chosen as this from aluminum or a transition metal element — expressing — it was able to obtain.

[0024]M in the above-mentioned general formula uses nickel or nickel as an essential ingredient, what added one sort or two sorts or more of metal chosen as this from aluminum or a transition metal element is expressed, and copper, cobalt, chromium, iron, vanadium, titanium, etc. are illustrated as a desirable transition metal.

[0025]If x separates from the range of $0 \leq x \leq 0.2$, sufficient capacity will not come out as a lithium cell. If y hardly appears but 5V field exceeds 0.6 by less than 0.2 on the other hand, since 5V fields will begin to decrease in number conversely, it is not desirable. Since the valence of manganese or the metal M will rise and capacity will decrease if structure breaks easily, a cycle characteristic gets worse and z exceeds 4.06, since the oxygen into which z forms the frame of Spinel structure by less than 3.94 runs short, it is not desirable.

[0026]Since Li_2O , Li_2MnO_3 , and NiMnO_3 will remain if heat treatment temperature shall be less

than 700 **, and LiMnO_2 of *****, etc. will appear if it exceeds 900 **, and it does not become spinel single phase, it is not desirable.

[0027]On the other hand, although the method in particular of producing mixed hydroxide of manganese and the metal M with a coprecipitation method is not limited, the method of indicating below, etc. can be used for it, for example, and it may use these together.

** After dissolving a manganese metal and the metal M with acid, such as sulfuric acid, chloride, and nitric acid, alkaline aqueous solutions, such as sodium hydroxide and a potassium hydrate, are added, and it neutralizes, and is referred to as predetermined pH.

** After adding acidic solutions, such as sulfuric acid, chloride, and nitric acid, to manganese salt, such as manganese sulfate, a manganese chloride, and manganese nitrate, and dissolving the mixture of the salt of the metal M in it, alkaline aqueous solutions, such as sodium hydroxide and a potassium hydrate, are added, and it neutralizes, and is referred to as predetermined pH.

[0028]A buffer for pH can also be used if needed. Mixed hydroxide of the generated manganese and the metal M may perform rinsing and desiccation if needed.

[0029]

[Example]Although a concrete example explains some examples of this invention below, these examples do not restrict this invention in any meanings.

[0030]First, the valuation method of this invention is explained. Evaluation of the battery characteristic was performed using the coin type cell of a laboratory scale.

[0031]That is, it mixed and what stuck to the anode n-methyl pyrrolidone, in addition the thing which produced the film on aluminum foil with the doctor blade method by pressure, and stuck the metal lithium board to a nickel mesh by pressure was made the polyvinylidene fluoride as positive active material, conductive carbon, and a binder with the negative electrode. The separator used LiPF_6 of 1M for that with which the electrolysis solution mixed EC (ethylene carbonate) and DMC (dimethyl carbonate) for the thing made from polypropylene to 1 to 1, having added as a supporting electrolyte. The characteristic of this cell is 25 ** and was measured as charge and discharge current density 0.2 mAh/g and the cut-off voltage 3.0–5.1V.

[0032]Weighing of a manganese metal and the metallic nickel was carried out so that it might be set to Mn:nickel=1.5:0.5 (it is [a mole ratio and the following] the same), and it was made to dissolve in 50% of the weight of a sulfuric acid solution. After adding ammonium chloride to this and adjusting pH to about 5, the sodium hydroxide solution of 4 mol/l was added and mixed hydroxide of manganese and nickel was made to coprecipitate. Hydroxide after coprecipitation was dried after rinsing several times. The obtained granular material was formed by the spherical and needlelike primary particle.

[0033]To this granular material, in addition, Li_2CO_3 was mixed so that it might be set to Li:Mn:nickel=1:1.5:0.5, and it heat-treated in the 10-hour atmosphere at 700–900 **.

[0034]NiO was not contained in obtained spinel type compound $\text{LiMn}_{1.5}\text{nickel}_{0.5}\text{O}_4$ as a result of the phase identification by an X diffraction. Tap density was 2.4 g/cm^3 and was almost the same as that of LiCoO_2 currently generally used. The coin type cell was produced using this compound, and the battery characteristic was evaluated.

[0035]Drawing 1 was a discharge curve of what was performed at 800 **, the plateau existed only in the 4.7V neighborhood and active material capacity became 120 or more mAh/g and a good value. The result was the same also about what was heat-treated on condition of others.

[0036]

[Comparative example 1] EMD, nickel hydroxide $\text{nickel}(\text{OH})_2$, and Li_2CO_3 were mixed so that it might be set to Li:Mn:nickel=1:1.5:0.5, and it heat-treated in the 10-hour atmosphere at 700–900 **. Remains of NiO were checked as a result of the phase identification by an X diffraction.

Drawing 2 is a discharge curve of the coin cell produced using what was heat-treated at 800 **. Since there were few 5V fields than Example 1 and their about 90 mAh/g was [nickel substitution by remains of NiO] insufficient, it is thought that 4V field also remained.

[0037]

[Comparative example 2] EMD, nickel hydroxide nickel(OH)_2 , and Li_2CO_3 were mixed so that it might be set to $\text{Li:Mn:nickel}=1:1.5:0.5$, and it heat-treated in the 100-hour atmosphere at 700–900 **. Although heat treating time was developed substantially, as a result of the phase identification by an X diffraction, remains of NiO were checked and the battery characteristic was the same as that of the comparative example 1.

[0038]

[Comparative example 3] EMD, nickel hydroxide nickel(OH)_2 , and Li_2CO_3 were mixed so that it might be set to $\text{Li:Mn:nickel}=1:1.5:0.5$, and it heat-treated in the 10-hour atmosphere at 900–1100 **. Although heat treatment temperature was raised, as a result of the phase identification by an X diffraction, LiMnO_2 of remains of NiO and ***** was checked and the battery characteristic was the same as that of the comparative example 1.

[0039]

[Comparative example 4] EMD, nickel hydroxide nickel(OH)_2 , and Li_2CO_3 were mixed so that it might be set to $\text{Li:Mn:nickel}=1:1.86:0.14$, $1:1.75:0.25$, $1:1.62:0.38$, and $1:1.5:0.5$, and it heat-treated in the 10-hour atmosphere at 800 **. As a result of the phase identification by an X diffraction, only in the case of $\text{Li:Mn:nickel}=1:1.86:0.14$, NiO was not detected, but, as for others, remains of NiO were checked. When the battery characteristic was measured, it was comparing with Example 1 like drawing 3, and 5V field also had few gaps.

[0040] As mentioned above, although the case where M of general formula $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ was nickel was explained as an example of representation, this invention does not receive restriction at all by this.

[0041]

[Effect of the Invention] As explained above, at this invention, it is general formula $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$, and M). nickel or nickel was used as the essential ingredient, and one sort or two sorts or more of metal chosen from aluminum or a transition metal element was added -- expressing -- in the manufacturing method of the positive electrode material for lithium secondary batteries which comprises the lithium inserted compound of the Spinel structure expressed, Manganese of a predetermined ratio and mixed hydroxide of the metal M are produced with a coprecipitation method, this is mixed with a lithium compound, and it heat-treats at 700 ** – 900 **.

Therefore, there are no remains of NiO and a 5V class spinel compound with high tap density can be obtained.

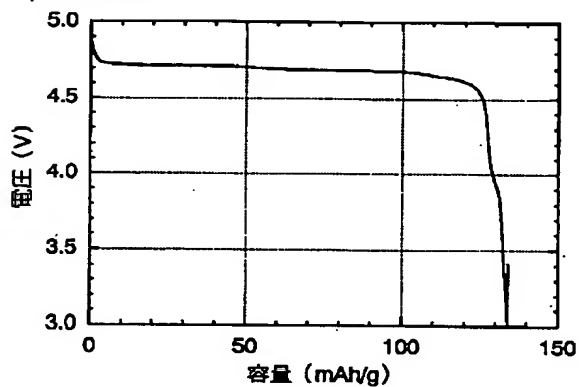
* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

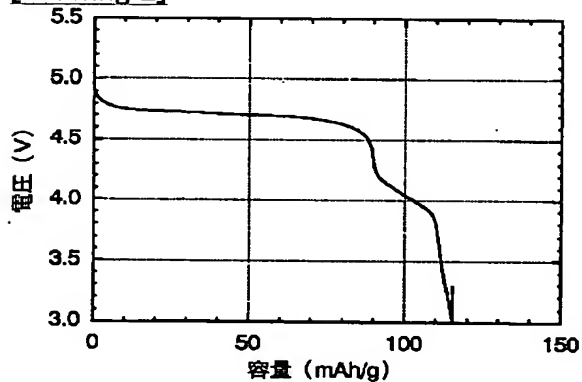
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

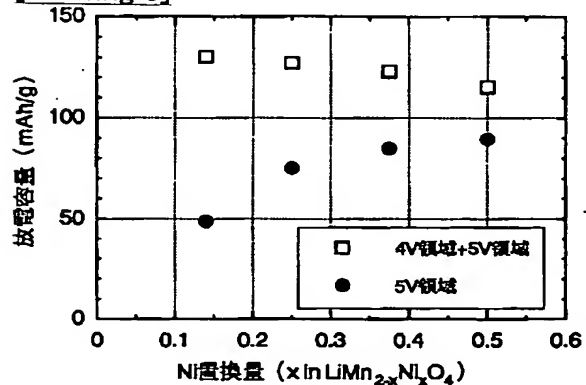
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2001-185145

(P2001-185145A)

(43) 公開日 平成13年7月6日(2001.7.6)

(51) Int.Cl.⁷

H 0 1 M 4/58

C 0 1 G 45/00

識別記号

F I

H 0 1 M 4/58

タームコード(参考)

4 G 0 4 8

5 H 0 0 3

機材ホビー
永田さん送付

請求項の数 2 O L (全 5 頁)

(21) 出願番号

特願平11-368613

(22) 出願日

平成11年12月27日(1999. 12. 27)

(71) 出願人 591007860

株式会社日鉱マテリアルズ

東京都港区虎ノ門2丁目10番1号

(72) 発明者 小廣 健司

茨城県北茨城市華川町白場187番地 4 株

株式会社日鉱マテリアルズ磯原工場内

(72) 発明者 藤平 善久

大阪府大阪市住吉区墨江4-1-29

(74) 代理人 100093296

弁理士 小越 勇

Fターム(参考) 4G048 AA04 AB01 AB05 AC06 AE05

5H003 AA02 AA08 BA01 BB05 BC01

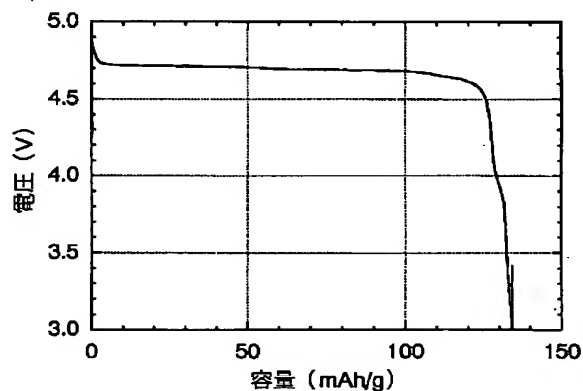
BC06 BD00 BD01

(54) 【発明の名称】 リチウム二次電池用正極材料の製造方法

(57) 【要約】

【課題】 NiOを含まない $Li_{(1+x)}Mn_{(2-x-y)}M_yO_4$ 系スピネル化合物を製造する方法を確立する。

【解決手段】 一般式 $Li_{(1+x)}Mn_{(2-x-y)}M_yO_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.96 \leq z \leq 4.06$, Mは、ニッケル又はニッケルを必須成分とし、これにアルミニウム又は遷移金属元素から選ばれる1種又は2種以上の金属を加えたものを表す) で表されるスピネル構造のリチウム挿入化合物から成るリチウム二次電池用正極材料の製造方法において、所定比のマンガンを金属Mの混合水酸化物を共沈法によって作製し、これをリチウム化合物と混合して700℃～900℃で熱処理することを特徴とする。



【特許請求の範囲】

【請求項1】 一般式 $Li_{(1+x)}Mn_{(2-x-y)}M_yO_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$ 、Mは、ニッケル又はニッケルを必須成分とし、これにアルミニウム又は遷移金属元素から選ばれる1種又は2種以上の金属を加えたものを表す) で表されるスピネル構造のリチウム挿入化合物から成るリチウム二次電池用正極材料の製造方法において、所定比のマンガンと金属Mの混合水酸化物を共沈法によって作製し、これをリチウム化合物と混合して700℃～900℃で熱処理することを特徴とするリチウム二次電池用正極材料の製造方法。

【請求項2】 上記遷移金属元素が、銅、コバルト、クロム、鉄であることを特徴とする請求項1記載のリチウム二次電池用正極材料の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、リチウム二次電池用正極材料、特に高電圧正極材料である $LiMn_2O_4$ 系スピネル化合物に関する。

【0002】

【0003】

【0004】

【0005】

【0006】

【0007】

【0008】

池電圧が高くなると特に電気自動車用など電池を数多く積層する必要がある場合に大きなメリットがある。

【0009】

【0010】

【0011】

【0012】

【0013】

【0014】

【0015】

【0016】

【0017】

【0016】

【課題を解決するための手段】本発明者らは、上記目的を達成するため、 $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ の製造方法について鋭意検討した結果、所定比のマンガンと金属Mの混合水酸化物を共沈法によって作製し、これをリチウム化合物と熱処理することにより、NiOが残留しないということを見いだした。

【0017】この知見に基づいて、本発明は、

(1) 一般式 $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$ 、Mは、ニッケル又はニッケルを必須成分とし、これにアルミニウム又は遷移金属元素から選ばれる1種又は2種以上の金属を加えたものを表す)で表されるスピネル構造のリチウム挿入化合物から成るリチウム二次電池用正極材料の製造方法において、所定比のマンガンと金属Mの混合水酸化物を共沈法によって作製し、これをリチウム化合物と混合して $700^\circ\text{C} \sim 900^\circ\text{C}$ で熱処理することを特徴とするリチウム二次電池用正極材料の製造方法、

(2) 上記遷移金属元素が、銅、コバルト、クロム、鉄であることを特徴とする前記(1)記載のリチウム二次電池用正極材料の製造方法、を提供する。

【0018】

【発明の実施の形態】以下、本発明の実施の形態について、詳細に説明する。本発明の最大の特徴は、一般式 $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$ 、Mは、ニッケル又はニッケルを必須成分とし、これにアルミニウム又は遷移金属元素から選ばれる1種又は2種以上の金属を加えたものを表す)で表されるスピネル構造のリチウム挿入化合物から成るリチウム二次電池用正極材料の製造方法において、予め、所定比のマンガンと金属Mの混合水酸化物を共沈法によって作製し、例えば、ニッケル・マンガンの複合水酸化物、ニッケル・アルミニウム・マンガンの複合水酸化物等とした後、これをリチウム化合物と混合して熱処理することにある。

【0019】一般式 $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ で表されるスピネル構造のリチウム挿入化合物は、基本的には、マンガン化合物、金属Mの化合物及びリチウム化合物を混合後、熱処理することで製造できるはずである。従って、本発明者等は、マンガン化合物、金属Mの化合物、リチウム化合物のそれぞれについて種々の化合物を使用して合成を試みた。例えば、マンガン化合物としては、 MnO_2 、 Mn_2O_3 、 MnCO_3 、 $\text{Mn}(\text{NO}_3)_2$ 等を、金属Mの化合物として、 $\text{Ni}(\text{OH})_2$ 、 NiO 、 $\text{Ni}(\text{NO}_3)_2$ 、 $(\text{COO})_2\text{Ni}$ 、 Co_3O_4 、 $\text{Co}(\text{OH})_2$ 、 CoCO_3 、 Cr_2O_3 、 $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ 、 FeOOH 、 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 、 CuO 、 $\text{Cu}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$ 、 $\text{Al}(\text{OH})_3$ 等を、リチウム化合物

として、 Li_2CO_3 、 LiOH 等を使用してみた。

【0020】ところが、いずれの場合も一般式 $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ の $y=0.2$ を超えるとNiOが残留することがわかった。これは文献に記載されている内容と一致する(J. Electrochem. Soc., Vol143, 1607 (1996))。

【0021】NiOが残留する理由の一つとして、 $\text{Li}_{(1+x)}\text{Mn}_2\text{O}_z$ を作製する温度の $700^\circ\text{C} \sim 900^\circ\text{C}$ で $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ とNiOが安定して存在する、言い換えれば熱力学的に $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ 単相にならない可能性がある。しかしながら、例えば、 $\text{Li}-\text{Mn}-\text{Ni}-\text{O}$ 系の詳細な相図は存在しないが、 $\text{Mn}-\text{Ni}-\text{O}$ 系の相図ではスピネル構造の $\text{Ni}_x\text{Mn}_2\text{O}_4$ の単相が、かなり広い領域で存在している。このことから推測すると、 $\text{Li}_{(1+x)}\text{Mn}_2\text{O}_z$ 作製温度でも、 $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ は単相で存在すると考えられる。

【0022】Ni-Oが残留するもう一つの理由として、反応性の違いが考えられる。すなわち、リチウム化合物とマンガン化合物がまず反応し、その後にニッケル化合物が反応する。ニッケル化合物の反応性が最も悪く、 $\text{Li}_{(1+x)}\text{Mn}_2\text{O}_z$ が初めにできてしまうと、ニッケル化合物との反応速度が著しく遅いためNiOが残留してしまうことになる。仮にこれが正しいとすると、マンガン化合物とニッケル化合物をまず熱処理し、その後リチウム化合物と反応させれば、NiOの残留を防止できる。さらに発展させれば、マンガン化合物とニッケル化合物が非常に均一に混合され、しかも、良好に接触していれば、リチウム化合物とマンガン化合物の反応の前にマンガン化合物とニッケル化合物が反応するはずである。

【0023】このような考えに基づき研究した結果、所定比のマンガンと金属Mの混合水酸化物を共沈法によって作製し、これをリチウム化合物と混合して $700^\circ\text{C} \sim 900^\circ\text{C}$ で熱処理することにより、NiOの残留しない $\text{Li}_{(1+x)}\text{Mn}_{(2-x-y)}\text{M}_y\text{O}_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$ 、Mは、ニッケル又はニッケルを必須成分とし、これにアルミニウム又は遷移金属元素から選ばれる1種又は2種以上の金属を加えたものを表す)を得ることが出来た。

【0024】上記一般式中のMは、ニッケル又はニッケルを必須成分とし、これにアルミニウム又は遷移金属元素から選ばれる1種又は2種以上の金属を加えたものを表し、好ましい遷移金属としては、銅、コバルト、クロム、鉄、バナジウム、チタン等が例示される。

【0025】なお、 x が $0 \leq x \leq 0.2$ の範囲を外れるとリチウム電池として、十分な容量が出ない。一方、 y が 0.2 未満では、 5V 領域がほとんど現れず、 0.6

を超えると、逆に5V領域が減少し始めるので好ましくない。又、 z が3.94未満では、スピネル構造のフレームを形成する酸素が不足するので、構造が壊れやすく、サイクル特性が悪化し、 z が4.06を超えるとマンガン又は金属Mの原子価が上昇し、容量が減少するので好ましくない。

【0026】又、熱処理温度を700℃未満とすると、 Li_2O 、 Li_2MnO_3 、 NiMnO_3 が残留し、又、900℃を超えると正方晶の LiMnO_2 等が出現し、スピネル単相とならないので好ましくない。

【0027】一方、マンガンと金属Mの混合水酸化物を共沈法によって作製する方法は、特に限定されるものではないが、例えば、以下に記載する方法等を用いることができ、これらを併用しても良い。

①金属マンガンと金属Mを硫酸、塩酸、硝酸等の酸により溶解させた後、水酸化ナトリウム、水酸化カリウム等のアルカリ水溶液を加えて中和して所定のpHとする。

②硫酸マンガン、塩化マンガン、硝酸マンガン等のマンガン塩に金属Mの塩の混合物に硫酸、塩酸、硝酸等の酸性溶液を加えて溶解させた後、水酸化ナトリウム、水酸化カリウム等のアルカリ水溶液を加えて中和して所定のpHとする。

【0028】なお、必要に応じ、pH緩衝剤を用いることもできる。又、生成したマンガンと金属Mの混合水酸化物は、必要に応じ、水洗、乾燥を行っても良い。

【0029】

【実施例】以下に、具体的な実施例によって本発明のいくつかの例を説明するが、これらの実施例はどのような意味においても本発明を制限するものではない。

【0030】まず、本発明の評価方法を説明する。電池特性の評価は、実験室規模のコイン型電池を用いて行った。

【0031】すなわち、正極活物質、導電性カーボン及び結着剤としてのポリフッ化ビニリデンに n -メチルピロリドン加えて混合し、ドクターブレード法でアルミ箔上に製膜したものを正極に、金属リチウム板をニッケルメッシュに圧着したものを負極とした。セパレーターはポリプロピレン製のものを、電解液はEC（エチレンカーボネート）とDMC（ジメチルカーボネート）を1対1に混合したものに支持塩として1Mの LiPF_6 を加えて使用した。この電池の特性は、25℃で、充放電電流密度0.2mAh/g、カットオフ電圧3.0～5.1Vとして測定した。

【0032】金属マンガンと金属ニッケルを $\text{Mn}:\text{Ni}=1.5:0.5$ （モル比、以下、同様である）となるように秤量し、50重量%の硫酸溶液に溶解させた。これに、塩化アンモニウムを加えてpHを約5に調整した後、4mol/lの水酸化ナトリウム溶液を添加して、マンガンとニッケルの混合水酸化物を共沈させた。共沈後の水酸化物は、数回水洗した後、乾燥させた。得られ

た粉体は、球状で針状の一次粒子により形作られていた。

【0033】この粉体に Li_2CO_3 を $\text{Li}:\text{Mn}:\text{Ni}=1:1.5:0.5$ となるように加えて混合し、700～900℃で10時間大気中で熱処理した。

【0034】X線回折による相同定の結果、得られたスピネル型化合物 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ にはNiOは含まれていなかった。又、タップ密度は、2.4g/cm³で、一般に使用されている LiCoO_2 とほぼ同様のものではあった。この化合物を使用してコイン型電池を作製し電池特性を評価した。

【0035】図1は、800℃で行ったものの放電曲線で、4.7V付近のみにプラトーが存在し、活物質容量は120mAh/g以上と良好な値となった。他の条件で熱処理したものについても結果は同様であった。

【0036】

【比較例1】EMDと水酸化ニッケル $\text{Ni}(\text{OH})_2$ 、 Li_2CO_3 を $\text{Li}:\text{Mn}:\text{Ni}=1:1.5:0.5$ となるように混合し、700～900℃で10時間大気中で熱処理した。X線回折による相同定の結果、NiOの残留が確認された。図2は800℃で熱処理したものを使用して作製したコイン電池の放電曲線である。5V領域は90mAh/g程度で実施例1より少なく、NiOの残留によるNi置換が不充分だったために、4V領域も残ったと考えられる。

【0037】

【比較例2】EMDと水酸化ニッケル $\text{Ni}(\text{OH})_2$ 、 Li_2CO_3 を $\text{Li}:\text{Mn}:\text{Ni}=1:1.5:0.5$ となるように混合し、700～900℃で10時間大気中で熱処理した。熱処理時間を大幅に伸ばしたが、X線回折による相同定の結果、NiOの残留が確認され、電池特性も比較例1と同様であった。

【0038】

【比較例3】EMDと水酸化ニッケル $\text{Ni}(\text{OH})_2$ 、 Li_2CO_3 を $\text{Li}:\text{Mn}:\text{Ni}=1:1.5:0.5$ となるように混合し、900～1100℃で10時間大気中で熱処理した。熱処理温度を上げたが、X線回折による相同定の結果、NiOの残留と正方晶の LiMnO_2 が確認され、電池特性も比較例1と同様であった。

【0039】

【比較例4】EMDと水酸化ニッケル $\text{Ni}(\text{OH})_2$ 、 Li_2CO_3 を $\text{Li}:\text{Mn}:\text{Ni}=1:1.86:0.14$ 、 $1:1.75:0.25$ 、 $1:1.62:0.38$ 及び $1:1.5:0.5$ となるように混合し、800℃で10時間大気中で熱処理した。X線回折による相同定の結果、 $\text{Li}:\text{Mn}:\text{Ni}=1:1.86:0.14$ の場合のみNiOが検出されず、他はNiOの残留が確認された。電池特性を測定したところ、図3の様に実施例1と比較していずれも5V領域は少なかった。

【0040】以上、一般式 $\text{Li}_{(1+x)}\text{Mn}$

$(2-x-y)M_yO_z$ のMがニッケルの場合を代表例として説明したが、本発明はこれによって、何ら制限を受けるものではない。

【0041】

【発明の効果】 以上説明したように、本発明は、一般式 $Li_{(1+x)}Mn_{(2-x-y)}M_yO_z$ ($0 \leq x \leq 0.2$, $0.2 \leq y \leq 0.6$, $3.94 \leq z \leq 4.06$, Mは、ニッケル又はニッケルを必須成分とし、アルミニウム又は遷移金属元素から選ばれる1種又は2種以上の金属を加えたもの表す) で表されるスピネル構造のリチウム挿入化合物から成るリチウム二次電池用正極材料の製造方法において、所定比のマンガンと金属Mの混合水酸化物を共沈法によって作製し、これをリチウム化合物と混合して700℃～900℃で熱処理することに

より、NiOの残留がなく、かつ、タップ密度の高い5V級のスピネル化合物を得ることができる。

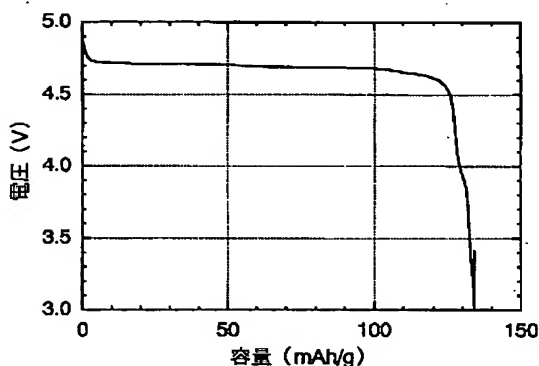
【図面の簡単な説明】

【図1】 図1は、実施例1で得られた $LiMn_{1.5}Ni_{0.5}O_4$ を用いて作製したコイン型電池の放電曲線を示すグラフである。

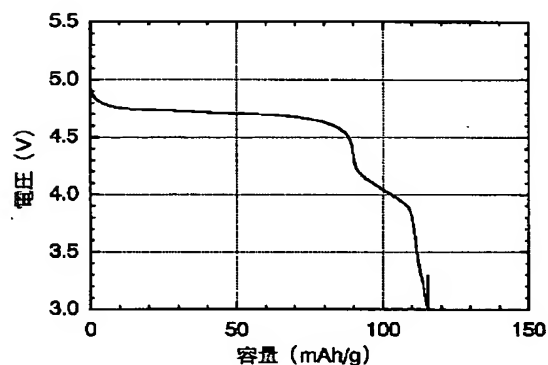
【図2】 図2は、比較例1、2で得られた $LiMn_{1.5}Ni_{0.5}O_4$ を用いて作製したコイン型電池の放電曲線を示すグラフである。

【図3】 図3は、比較例3で得られた $LiMn_{2-x}Ni_xO_4$ を用いて作製したコイン型電池の放電容量の内、4V領域と5V領域を加えた容量と5V領域のみの容量を示すグラフである。

【図1】



【図2】



【図3】

